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Chemical generation of atomic iodine for COIL

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ABSTRACT

A method of the chemical production of atomic iodine aimed for application in COIL was studied experimentally. The method is based on chemical generation of chlorine atoms and their subsequent reaction with hydrogen iodide. Effects of initial ratio of reactants and the way of their mixing were investigated and interpreted by means of the developed model of the reaction system. In optimum conditions, the yield of iodine atoms, related to HI, attained 70 – 100 %.

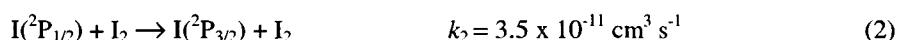
Keywords: atomic iodine, atomic chlorine, chemical oxygen-iodine laser, COIL,

1. INTRODUCTION

In conventional COIL systems, the energy of 4-6 molecules of singlet oxygen, $O_2(^1\Delta_g)$, is consumed to dissociate one iodine molecule to iodine atoms



In the case of another source of atomic iodine, this energy might be utilized for laser pumping. It was estimated that a production of atomic iodine without participation of singlet oxygen could increase a laser power by 25 %.¹ Molecular iodine as a precursor of iodine atoms in COIL introduces further drawbacks like a very fast quenching of excited iodine atoms by iodine molecules



or technical problems connected with evaporation of solid or liquid iodine and supplying iodine vapor into the laser mixing region. To avoid the process (1), methods of microwave discharge pre-dissociation of iodine molecules,² or dissociation of alkyl iodides by electrical discharge³ were investigated up to now. We proposed a method of chemical generation of atomic iodine that fit to COIL conditions.^{4,5} In this paper, results of experimental investigation are presented.

2. DESCRIPTION OF REACTION SYSTEM

The proposed method of chemical generation of atomic iodine in COIL takes advantage of the knowledge gathered during investigation of chemical HCl and HCl/CO₂ transfer lasers.⁶ It is based on a two-step process. In the first step, atomic chlorine is formed by the reaction of chlorine dioxide with nitrogen oxide, in the second step chlorine atoms react with gaseous hydrogen iodide producing atomic iodine.

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2.1 Generation of chlorine atoms

The fast exothermic reaction of gaseous chlorine dioxide with nitrogen oxide



is employed to generate Cl atoms. It proceeds as a branched chain reaction consisting of the following steps



Reaction (6) is the chain-branched step since there is a net production of one chain carrier. The main reaction product is atomic chlorine for the initial NO : ClO₂ ratio equal to 2 : 1, or ClO radicals for the ratio 1 : 1, respectively. For a fast and efficient course of the above process, the chain carriers Cl and ClO must not be excessively depleted by other processes. The most important loss processes for both Cl and ClO are the termolecular reactions with nitrogen dioxide, NO₂, which is an unavoidable and stable by-product of the reactions (4) and (5)^{6,7}



2.2. Generation of iodine atoms

Iodine atoms are generated by the very fast exothermic reaction of chlorine atoms with hydrogen iodide



In this reaction, up to 70 % of the reaction exothermicity is transferred into vibrational energy of HCl* molecules.⁶ In the case of atomic iodine generation in the stream of singlet oxygen, iodine atoms will be excited in the reaction



Besides this process, recombination of iodine atoms into molecules takes place in termolecular reaction with helium ($k_{12} = 3.8 \times 10^{-33} \text{ cm}^6 \text{s}^{-1}$), and molecular iodine ($k_{13} = 3.7 \times 10^{-30} \text{ cm}^6 \text{s}^{-1}$), respectively. The most important loss process for atomic iodine, owing to a high concentration of NO₂ in the reaction mixture, is the reaction with nitrogen dioxide



followed by



The modeling neglecting a limited mass-transfer rate showed^{6,7} that simultaneous injection of HI, ClO₂ and NO is characterized by exhausting Cl atoms from the reaction mixture by the extremely fast reaction with HI, which results in deceleration of the chain reaction (3). Admixing of hydrogen iodide at a certain distance downstream from the mixing point of ClO₂ and NO was found to be more effective for atomic I production.⁷ A partitioning of NO flow between two injectors was proposed because it could also diminish a loss of produced chlorine atoms⁶. An optimum yield of iodine

atoms was obtained when the second half of NO with HI was injected 0.6 cm downstream from the first injection place (at gas velocity of 200 m s^{-1}).⁷

3. EXPERIMENTAL

The generation of atomic iodine was studied in the system with nitrogen, and some preliminary experiments were performed in the flow of singlet oxygen. A small-scale device was designed for the flow and pressure conditions that are characteristic for the subsonic flow upstream the supersonic nozzle in COIL. The setup for measurements in an excess of nitrogen is shown schematically in Fig. 1.

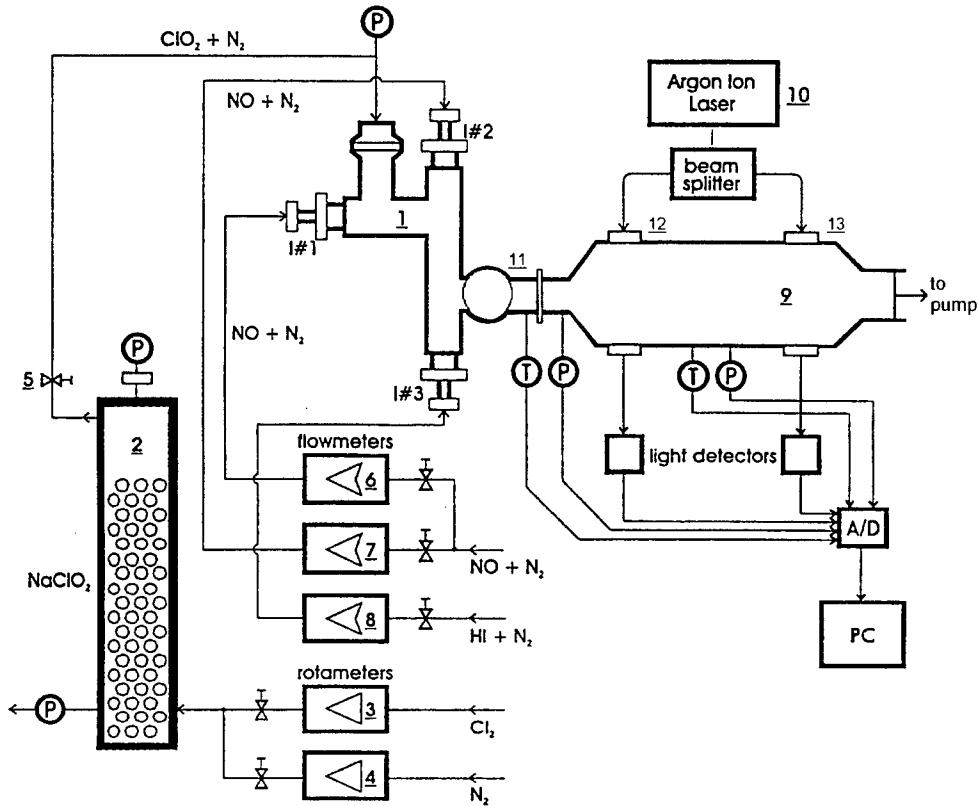


Fig.1. Scheme of the small-scale device for atomic iodine generation. 1 – flow reactor, 2 – ClO_2 generator, 3,4 – rotameters, 5 – valve, 6 – 8 flowmeters, 9 – diagnostics cell, 10 – Ar ion laser, 11 – ISD cell, 12, 13 – VIS photometry cells

A flow-through chemical reactor 1 is made of stainless steel tube of 10 mm in inner diameter. In the reactor bends, three injectors are inserted coaxially for injection secondary gases into the primary gas. They can be moved and so allow to adjust a time span between injection of reactants. The injectors are made of stainless steel tube of 5 mm in outer diameter with one, two or three rows of openings. The reactor was designed for the flows: 0.1 mmol ClO_2 + 5 mmol N_2/s as a primary flow, 0.1 mmol NO/s + 1 mmol N_2/s through the 1st and 2nd injector, respectively, 0.1 mmol HI/s + 1 mmol N_2/s through the 3rd injector. Diameter and number of the openings in each injector were calculated so to assure the full penetration of each secondary gas into the primary flow. 24 openings of 0.4 mm in diameter were drilled in the 1st injector, 20 openings in the 2nd injector, and 16 openings in the 3rd injector. The pressure in each injector, and the

pressure before the measuring diaphragm of flowmeters 6 – 8 matched up the sonic condition in the diaphragm orifice. The pressure in the reactor was 2 – 4 kPa (15 – 30 torr) and the gas velocity 140 m s⁻¹.

The primary gas flowing into the reactor contained 4 - 10 % ClO₂. A mixture of NO and nitrogen (10 % NO) was introduced either through the 1st and 2nd injectors simultaneously, or through one of them only. The mixture of hydrogen iodide and nitrogen (with 8 - 10 % HI) was mostly introduced through the 3rd injector. Flow rates of reacting gases were up to 240 μmol ClO₂/s, 600 μmol NO/s and 500 μmol HI/s.

Gaseous chlorine dioxide, the reactant for chlorine atoms formation, was produced on site by a heterogeneous reaction between gaseous chlorine and sodium chlorite⁶



This process took place in the ClO₂ generator 2, where gaseous chlorine diluted with nitrogen (in the ratio from 1 : 20 to 1 : 50) was introduced at room temperature. The generator made of PVC tube (7 cm or 11 cm of inner diameter, 1 m long) was filled with either powdered sodium chlorite, or water solution of this salt (40 % w/w). For safety reasons, the partial pressure of ClO₂ in the system should not exceed 30 torr. Flow rates of chlorine dioxide and residual chlorine were determined by chemical analysis of the solution obtained by bubbling the exiting gas through a solution of potassium iodide.

Gas mixture exiting the reactor 1 entered first the optical cell 11 used for atomic iodine detection by the Iodine Scan Diagnostics (ISD) with a tunable diode probe laser.⁸ The method is based on the sensitive absorption spectroscopy by means of tunable near infrared diode laser that monitors the gain or absorption for the I(²P_{1/2}) - I(²P_{3/2}) transition at 1315 nm. The laser frequency is scanned over the 3–4 transition in iodine atom. The probe beam passes through the optical cell 11 (11 mm in inner diameter and 45 mm of inner length) in the double pass configuration parallel to the gas flow direction. The optical cell was attached to the reactor without any connecting tube as the lifetime of iodine atoms in the studied gas mixture is rather short (0.1 – 1 ms).⁷ Due to low flow rates of reactants and produced atomic iodine, and because a sufficient absorption length was needed, the longitudinal gas flow through the cell was chosen. The gain/loss data were processed with PC on line using a special developed software. Besides this direct method for I atoms detection, an indirect method was used based on the measuring the concentration of I₂ molecules that are formed by recombination of generated iodine atoms at some distance downstream. The I₂ concentration was determined by the VIS photometry at 488 nm in two optical cells 12, and 13. The argon ion laser with a beam splitter, two silicon photodiodes, and current amplifiers were used. Signals from these diodes, signals from the gas flow meters 6 – 8, and temperature and pressure sensors were processed by AD converter and PC on line. The transport time of gas from the 3rd injector to the entrance of the cell 11 was about 0.2 ms, to the cell exit 0.8 ms, to the axis of the cell 12 – 6 ms, and to the axis of the cell 13 - 93 ms, respectively. The flow rate of produced nitrogen dioxide was evaluated from the change of 488 nm light absorption after admixing NO into the primary ClO₂ flow (before HI admixing) using the published absorption cross-section of 2.7 × 10⁻¹⁹ cm². Gas exiting the diagnostic cell was passed through a scrubber with a bed of solid potassium hydroxide and through a liquid nitrogen trap. The system was exhausted with a rotary pump (25 m³/h).

A generation of atomic iodine in the flow of singlet oxygen was performed using the same reactor 1, into which a stream of singlet oxygen was introduced as the primary gas. A small-scale jet-type generator of the cross section 8 × 16 mm with liquid jets counter-flown by gaseous chlorine was described in detail in our earlier paper.⁹ The O₂(¹Δ_g) concentration was evaluated from 1.27 μm emission in a detection cell placed at the generator exit. The gas containing O₂(¹Δ_g) was introduced into the reactor 1 as a primary gas, the mixture ClO₂ + N₂ was injected through the 1st injector, NO + N₂ through the 2nd injector, and HI + N₂ through the 3rd injector.

4. RESULTS AND DISCUSSION

4.1. ClO₂ production

A solid NaClO₂ (50% w/w) was used first for ClO₂ production. The larger ClO₂ generator was filled with 10 dm³ of powdered chlorite, and 90 μmol chlorine/s was passed through it. It produced 140 – 150 μmol ClO₂/s with the yield of 80 – 85 %, the exiting gas contained further about 15 μmol/s of residual chlorine. At higher chlorine flow rate, the ClO₂

yield was lower. The ClO_2 yield was also decreasing with "aging" the filler (e.g., only 40 % yield was measured after two months of intermittent use, even if the sodium chlorite was exhausted from 12 – 15 % only). This phenomenon, observed also by Arnold⁶, is probably caused by a layer of sodium chloride on the surface of chlorite crystals. This layer obviously hinders the chlorine diffusion and slows down the ClO_2 production. In the second arrangement, chlorine-nitrogen mixture was bubbled through 1 dm³ of chlorite solution (32 %) providing 200 – 250 μmol ClO_2/s with the yield 81 – 85 %. The production rate was very stable for about 5 hours, which corresponded to about 90 % utilization of the chlorite. This process is substantially more effective and reproducible than the former. Some problem could introduce water in the exiting gas due to the quenching of excited iodine atoms. This effect, however, should not be too serious, as the contribution of this water is substantially lower than the amount produced by the singlet oxygen generator.

4.2. Molecular iodine formation

Besides molecular iodine formed by recombination of generated I atoms, some I_2 molecules may be formed also by other reactions. One of them is the reaction of residual molecular chlorine (coming from ClO_2 generator) with hydrogen iodide



The rate constant of this reaction $k_{15} = (3.4 \pm 1.7) \times 10^{-33} \text{ cm}^6 \text{s}^{-1}$ was evaluated from our earlier measurements⁴ performed in the described reactor at room temperature and concentration of reactants $(2 \div 9) \times 10^{16} \text{ cm}^{-3}$. It was found by the modeling of the reaction system producing atomic iodine that the reaction (15) may have some effect on the I_2 concentration measured in the optical cell 13, but effect of this reaction on the I_2 concentration in the cell 12 is negligible. For this reason, the overall rate of atomic iodine production was calculated from the I_2 flow rate evaluated for the cell 12.

In the next experiments the $\text{ClO}_2 - \text{HI}$ system was investigated. In the reactor 1, the secondary flow of 90 – 340 μmol HI/s was injected through the 3rd injector into the primary flow of 200 – 250 μmol ClO_2/s . No iodine atoms were detected in ISD cell 11, but molecular iodine was measured in both cells 12 and 13. From these measurements, the rate constant of the reaction



was evaluated. It followed from the modeling of the reaction system $\text{ClO}_2 - \text{NO} - \text{HI}$ that the reaction (16) may increase I_2 concentration measured in the cell 12. It occurred, however, only in the case of excessive HI flow rate against the rate of Cl atoms generation, i.e. at $\text{HI}/\text{ClO}_2 \geq 1$, and $\text{NO}/\text{ClO}_2 < 1$.

4.3. Atomic iodine generation in an excess of nitrogen

In Fig.2, an example of the time course of flow rates of HI and produced atomic iodine is shown for constant flow of nitrogen oxide. Atomic iodine was detected both directly by ISD, and indirectly as molecular iodine. It can be seen in this figure that the rate of generation of atomic iodine increases with increasing flow rate of hydrogen iodide. The flow rate of atomic iodine detected by ISD corresponded to the overall atomic I flow rate, however, up to about 50 $\mu\text{mol}/\text{s}$ only. With increasing HI flow rate above this limit, the ISD signal remained constant or even fell. This can be explained so that with increasing HI flow rate the rate of formation of atomic iodine also increases, and the rate of reactions (12), (13) as well. The local concentration of I atoms drops markedly with the distance from the HI injection,

and the flow rate measured by ISD represents only a fraction of the overall production rate. In these conditions the concentration gradient of atomic iodine downstream the HI injector may become steeper, and the fraction of the atomic iodine flow rate detected in the cell 11 to the overall production rate smaller. Fig. 3 shows a calculated course of atomic and molecular iodine flow rate downstream the HI injection. It can be seen that the average flow rate of atomic iodine in the ISD cell is substantially lower than the maximum flow rate near the HI injector. In a real system, the concentration gradient is probably more moderate due to a limited mass transfer rate. Results of modeling showed that the overall production rate of atomic iodine corresponds better to a double value of the molecular iodine flow rate

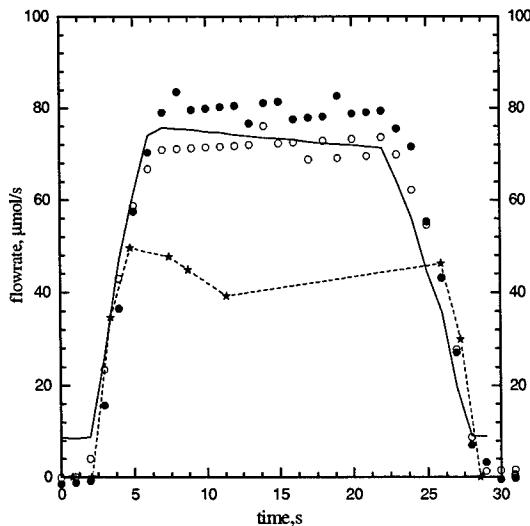


Fig.2: Time course of HI flow rate (—), rate of formation of atomic iodine detected by ISD (---★---), and visible photometry in the cells 12 (○) and 13 (●), respectively.
 Total pressure 2.1 kPa, 245 $\mu\text{mol ClO}_2/\text{s}$ and 2 mmol N_2/s in the primary flow, 150 $\mu\text{mol NO/s}$ through the 1st injector, 150 $\mu\text{mol NO/s}$ through the 2nd injector, $d_{1-2}=38 \text{ mm}$, $d_{2-3}=3.7 \text{ mm}$, $d_{3-\text{ISD}}=10 \text{ mm}$

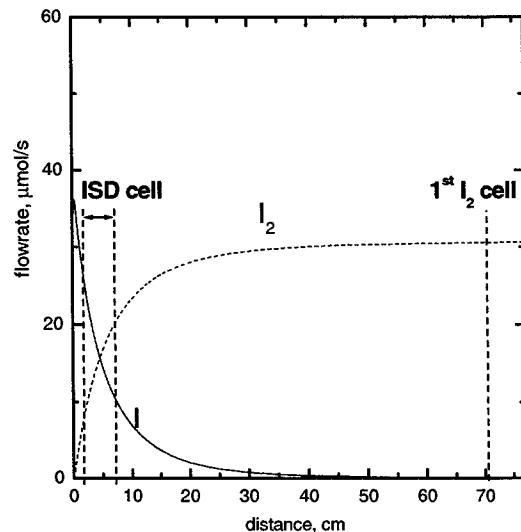


Fig.3: Calculated course of atomic and molecular iodine flow rate on the distance from the 3rd injector at gas velocity 140 m/s, 220 $\mu\text{mol ClO}_2/\text{s}$ in primary flow, 205 $\mu\text{mol NO/s}$ (2nd injector) and 220 $\mu\text{mol HI/s}$ (3rd injector), $d_{2-3}=3.7 \text{ mm}$, $d_{3-\text{ISD}}=11 \text{ mm}$.

measured in the cell 12. It is valid, however, only in the case that the contribution of the reaction (16) to the I_2 concentration can be neglected.

In the next experiments, approximately the same overall amount of NO was injected into the primary flow of chlorine dioxide, but in a different way. Nitrogen oxide was introduced either through 1st or 2nd injector, or through both injectors simultaneously (see Tab.I).

Table I

Effect of the way of NO injection on atomic I production measured by ISD ($n_{\text{I}}^{\text{ISD}}$) and VIS photometry ($n_{\text{I}}^{\text{VIS}}$). Primary flow 220 $\mu\text{mol ClO}_2/\text{s}$, distance between injectors: $d_{1-2}=30 \text{ mm}$, $d_{2-3}=3.7 \text{ mm}$, and to ISD cell 11: $d_{3-\text{ISD}}=20 \text{ mm}$.

n_{NO} (1 st inj.), $\mu\text{mol}/\text{s}$	n_{NO} (2 nd inj.), $\mu\text{mol}/\text{s}$	n_{HI} (3 rd inj.), $\mu\text{mol}/\text{s}$	$n_{\text{I}}^{\text{ISD}}$, $\mu\text{mol}/\text{s}$	$n_{\text{I}}^{\text{VIS}}$, $\mu\text{mol}/\text{s}$
320	0	100	0	18
150	150	100	50	80
0	330	100	82	98

When all NO was introduced through the 1st injector, most of Cl atoms were lost (by reactions (7) - (9)) before mixing with HI, which resulted in a low production of atomic iodine. A medium atomic iodine production was attained when NO was introduced through both 1st and 2nd injector simultaneously. Results of mathematical modeling of this system show (Fig. 4) that mostly ClO radicals are formed downstream the first injector (by the reaction (4)), and Cl atoms are generated downstream the second injector (by the non-chain mechanism). In this case, the HI injector was placed as close to the 2nd NO injector as possible so that a very small proportion of Cl atoms sufficed to be recombined in

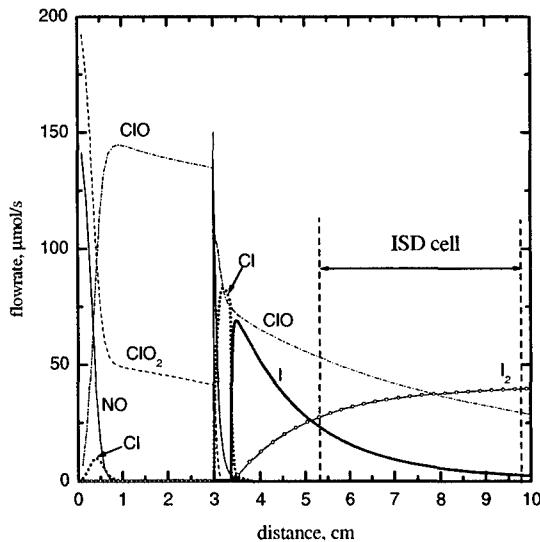


Fig.4: Calculated flow rate of reactants and products at gas velocity 140 m/s, 200 $\mu\text{mol ClO}_2/\text{s}$ in primary flow, 150 $\mu\text{mol NO}/\text{s}$ (1st injector), 150 $\mu\text{mol NO}/\text{s}$ (2nd injector) and 100 $\mu\text{mol HI}/\text{s}$ (3rd injector), $d_{1-2} = 38 \text{ mm}$, $d_{2-3} = 3.7 \text{ mm}$, $d_{3-ISD} = 20 \text{ mm}$

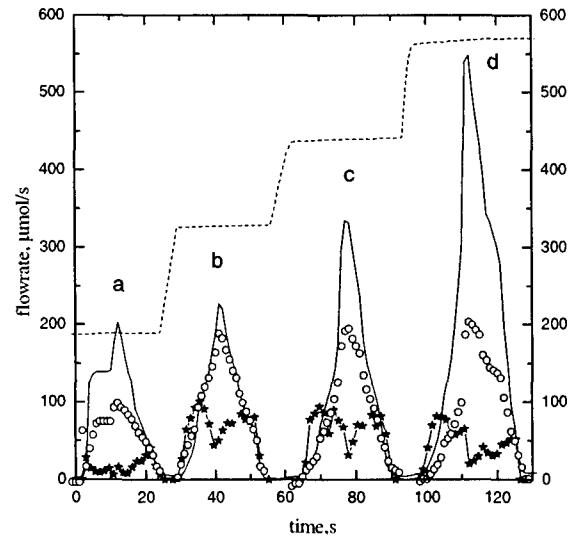


Fig.5 : Time course of NO flow rate through the 2nd injector (-----) and HI flow rate through the 3rd injector (—), rate of formation of atomic iodine detected by ISD in the cell 11 (—★—) and visible photometry in the cell 12 (○), respectively. Total pressure 2.1 kPa, 220 $\mu\text{mol ClO}_2/\text{s}$ and 2 $\text{mmol N}_2/\text{s}$ in the primary flow, $d_{1-2} = 38 \text{ mm}$, $d_{2-3} = 3.7 \text{ mm}$, $d_{3-ISD} = 10 \text{ mm}$.

reactions (7) - (9). This figure also shows that only a small fraction of I atoms can be detected by ISD cell. In a real system, this fraction may be higher due to a limited mass transfer rate that extends the region of iodine atoms further

downstream. It was also proved experimentally that the rate of I atoms production did not depend on the distance between the 1st and 2nd injector (in the range of 8-21 mm). This is in accordance with the calculated high stability of ClO radicals in this region (see Fig.4).

The highest yield of atomic iodine (measured by both methods) was achieved when all NO was injected only 3.7 mm upstream the HI injector. It means that the time span of 27 μs between 2nd and 3rd injector, respectively, is sufficient for an effective production of chlorine atoms formed by the chain mechanism of the reaction (3). This is in a good agreement with the time span of 35 μs system between the HI injection and the maximum concentration of Cl atoms which was obtained by the modeling (see Fig. 4 in our previous paper⁷).

In the next series, effects of distances between injectors on atomic iodine production were studied (see Tab. II).

Table II

Effect of distance between injectors, (d), on atomic I flow rate measured by ISD (n_I^{ISD}) and VIS photometry (n_I^{VIS}). Primary flow 240 $\mu\text{mol ClO}_2/\text{s}$, 1st injector: 220 $\mu\text{mol NO}/\text{s}$, 2nd injector: 220 $\mu\text{mol NO}/\text{s}$, 3rd injector: 100 $\mu\text{mol HI}/\text{s}$.

d_{1-2} , mm	d_{2-3} , mm	$d_{3-cell\ 11}$, mm	n_I^{ISD} , $\mu\text{mol /s}$	n_I^{VIS} , $\mu\text{mol /s}$
9	23	20	5	15
37	3.7	20	20	54
37	3.7	11	40	55

This data proved that diminishing the distance, d_{2-3} , between the second NO injector and HI injector is favorable (in spite of the longer distance between 1st and 2nd NO injection) due to a reduced loss of chlorine atoms. A diminishing of the distance between HI injection and ISD cell 11 resulted in higher concentration of I atoms measured in this cell even

though the overall rate of I generation remained unchanged. It can be explained by a lower loss of I atoms in reactions (12), (13). This result can also explain a very low ISD signal of atomic iodine measured during our initial experiments, when the ISD cell was connected with the reactor by means of a 4 cm long tube.

Another example of the measured time course of reactants and atomic iodine flow rate is shown in Fig. 5. This figure documents effects of HI and NO flow rate, respectively, on the production of atomic iodine. In accordance with the above results, a lower rate of I production was measured in the region *a*, when NO was introduced by the first and the second injector simultaneously.

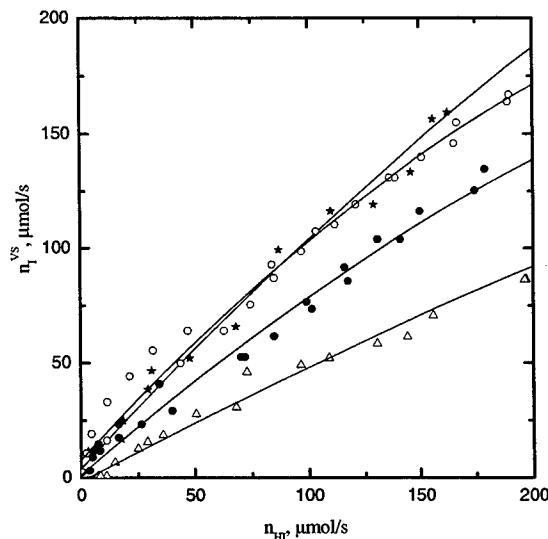


Fig. 6.: Overall flow rate of atomic iodine (in cell 12) on HI flow rate. NO flow rate: 205 $\mu\text{mol/s}$ (★), 330 $\mu\text{mol/s}$ (○), 440 $\mu\text{mol/s}$ (●), 560 $\mu\text{mol/s}$ (△), other conditions as in Fig.5.

very fast reaction (10), and further chlorine atoms are produced by the reaction (17). Excessive ClOO radicals then also provide Cl atoms in the reaction⁶



The modeling of this system showed that the atomic chlorine production by the chain reaction (3) (at $\text{NO}/\text{ClO}_2 \approx 2$) followed by atomic iodine formation (eq.(10)) proceeds much faster than the non-chain process through the reactions (4), (17), (18), and (10). In a real system, where the mixing of Cl atoms with HI occurs in a limited rate only, the second reaction path may be more effective because of lower loss of atomic chlorine in reactions (7) and (8). These loss processes proceed mostly in the regions with insufficient HI supply. The developed one-dimensional model (assuming an instantaneous mixing of reactants) of the studied reaction system, however, did not confirm quantitatively the observed effect of NO/ClO_2 ratio on the atomic iodine production.

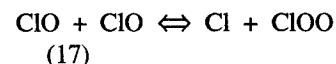
First experiments with atomic I generation in the flow of singlet oxygen are under way so that the preliminary results will be presented at the conference only.

4.5. Application possibilities of the method in COIL

The method of atomic iodine generation above described is planned to be applied in COIL provided that results of the study performed in the flow of singlet oxygen will be promising. Owing to a relatively short lifetime of iodine atoms in the reaction mixture (0.1 - 1 ms) at pressures typical for the subsonic part of COIL (a few kPa), an application of the proposed process is anticipated either very close to the supersonic nozzle, or with transonic mixing of reactants.

In the next regions, with NO introduced through the second injector, the overall rate of atomic iodine production was higher at lower NO/ClO_2 ratio. This is more obvious from the dependence of the production rate of I atoms on HI flow rate plotted for different NO flow rate (see Fig.6).

For NO/ClO_2 ratio equal to 1 or 1.5, the yield of atomic iodine was nearly 100 % (related to HI). At higher NO/ClO_2 ratio (2 and 2.6) the yield was substantially lower (70 and 45 %, respectively). This effect could be explained by different mechanism of atomic chlorine production in both experimental conditions. At $\text{NO}/\text{ClO}_2 \geq 2$, chlorine atoms are formed very fast by the chain branching mechanism (4) - (6) and still before mixing with HI may be partly lost by the fast reactions with nitrogen dioxide (eqs.(7), (8)). In the case of the ratio $\text{NO}/\text{ClO}_2 \approx 1$, more stable radicals ClO are formed, which are in equilibrium with Cl atoms and ClOO radicals⁶



This equilibrium is strongly shifted to the left ($k_{17} = 2.8 \times 10^{-14} \text{ cm}^3 \text{s}^{-1}$ and $k_{-17} = 1.0 \times 10^{-11} \text{ cm}^3 \text{s}^{-1}$). In the presence of HI, chlorine atoms are consumed in the

5. CONCLUSIONS

A method of the chemical production of atomic iodine, based on chemical generation of chlorine atoms and their subsequent reaction with gaseous hydrogen iodide, was studied experimentally. It is aimed to be applied it in the COIL operation. The method is.

Effects of initial ratio of reactants and the way of their mixing were studied and interpreted by means of the developed model of this reaction system.

In optimum conditions, the yield of atomic iodine production was rather high, from 70 to 100 % (related to ClO₂ or HI).

The proposed process of atomic I generation is assumed to be applied in the supersonic COIL either very close to a supersonic nozzle, or with transonic mixing of reactants. It may save a significant fraction of singlet oxygen and so increase the laser efficiency.

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